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RADIO CORPORATION OF AMERICA RCA LABORATORIES

THIRD QUARTERLY REPORT

THIN-FILM LARGE AREA PHOTOVOLTAIC SOLAR ENERGY CONVERTER

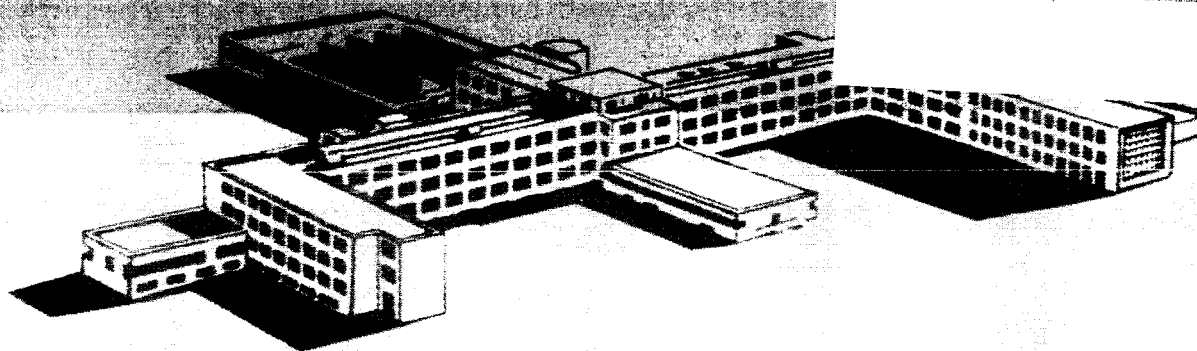
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DAVID SARNOFF RESEARCH CENTER
PRINCETON, NEW JERSEY

THIRD QUARTERLY REPORT)

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APRIL 1, 1963 TO JUNE 30, 1963

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PHOTOVOLTAIC SOLAR ENERGY CONVERTER

*Third
3rd Quarterly*

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RADIO CORPORATION OF AMERICA,
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PURPOSE

The objective of the program is to investigate materials and methods for the fabrication of large area solar cells.

ABSTRACT

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Experiments have been done on junctions in polycrystalline GaAs to *auth* clarify the effect of intercrystalline boundaries. As the skin resistance of a cell is reduced, the leakage becomes unacceptably high.

Cuprous iodide forms a photovoltaic barrier on n-type GaAs. Work has been directed at optimizing this system. A start has been made on exploring other barrier systems.

GaP on GaAs structures have been made. They do not all behave like heterojunctions.

AUTHOR

FACTUAL DATA

I. INTRODUCTION

Some experiments have been started which were aimed at measuring the effects of intercrystalline boundaries in polycrystalline GaAs photovoltaic junctions.

Since a powder cell may have special advantages in a large area structure, techniques are being evolved which can be applied to barrier formation in such cells. In particular, the barrier between cuprous iodide (CuI) and n-type GaAs has been studied.

A series of GaP on GaAs barriers have been made. These do not all behave in the expected fashion.

It may be helpful if we define at this point our usage* of the words "barrier" and "heterojunction". By "barrier" we mean a rectifying structure resulting from the contact of two dissimilar chemical phases. By "heterojunction" we mean that special form of "barrier" where the junction exists at, or on both sides, of the chemical interface.

II. GRAIN BOUNDARY EXPERIMENTS

On pages 1 and 2 of the Second Quarterly Report, reasons were given for believing that intercrystalline boundaries were responsible for the "softness" of junction characteristics in polycrystalline material. The studies reported there were made on junctions formed by changing the conditions of growth to change the conductivity type of the deposit.

* Usage in this report and following ones. Previous monthly and quarterly reports have been less precise in this respect.

Junctions formed by Zn diffusion into n-type GaAs could have the advantage of a more uniform junction depth (except perhaps at and near inter-crystalline boundaries) and a lower sheet resistance, as compared with grown junctions. Experiments were therefore undertaken to determine optimum diffusion conditions for polycrystalline material.

Slices of polycrystalline melt-grown n-type GaAs were exposed to Zn vapor at a fixed temperature for ten minutes. V_{oc} was then measured under standard illumination. Observations of the V-I characteristic were less revealing since pressure contacts were used. To obtain a corresponding V_{oc} for single crystal material, mesas were etched in regions away from the inter-crystalline boundaries and the measurements were repeated.

Figure 1 shows how V_{oc} varies with the temperature of diffusion for different original carrier concentrations in the n-type material. The crystal sizes used in these experiments were many millimeters in lateral extent.

The fall-off in V_{oc} with increasing temperature of diffusion may be explained in the following way. Consider two crystals, A and B of Figure 2, with a common boundary and suppose that this boundary provides a leakage path at the junction. If now an ohmic contact C is made to crystal B, the overall junction performance will be increasingly degraded as the sheet resistance of the p-type layer is reduced. It was in fact observed in the above experiments that the I-V characteristic for the polycrystalline junctions became less rectifying as the diffusion temperature was increased.

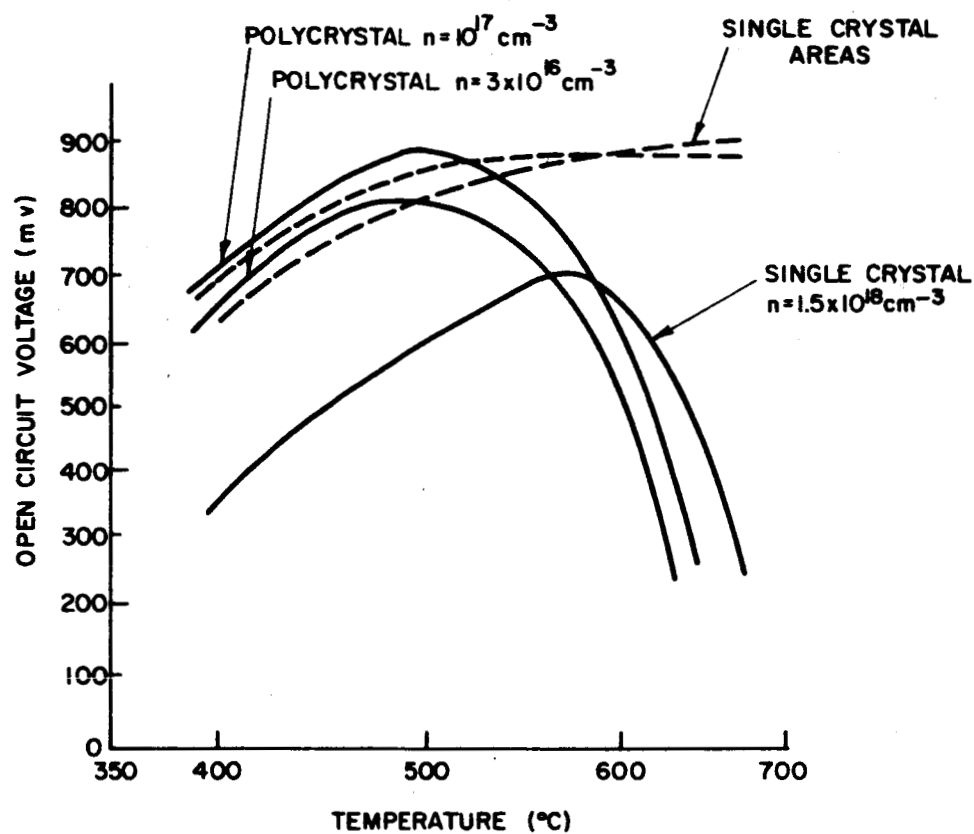


Fig. 1 V_{oc} as a function of temperature

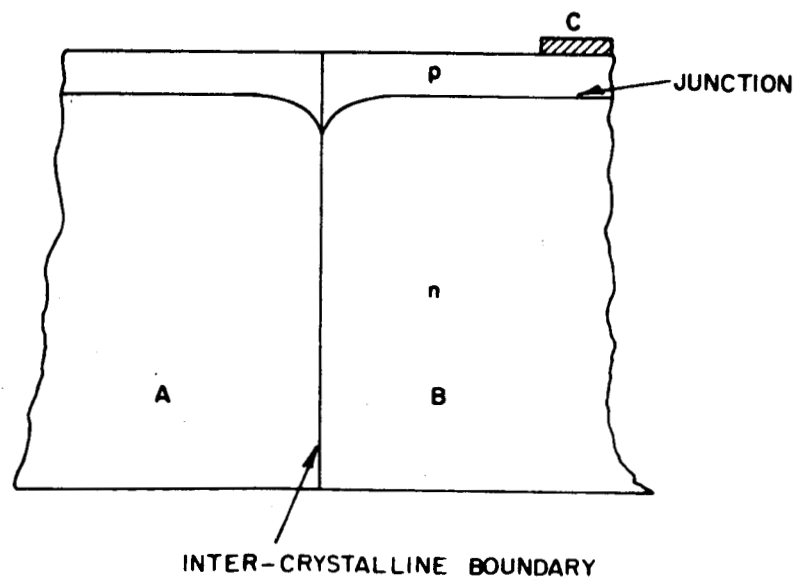


Fig. 2 Two-crystal model with a common boundary

Reverting again to Figure 2, there is presumably some distance L from the intercrystalline boundary over which the local photovoltaic efficiency, η , of the junction is less than a required efficiency, η_R , for the whole cell. L will be a function of the sheet resistance of the p-type layer, and also of the character of the intercrystalline boundary. Even when the local efficiency η is higher than η_R at places well removed from such a boundary, it is clear that the minimum acceptable crystal size in such a polycrystalline device will be large compared with L .

Experiments have been started to measure L for different crystal boundaries and junction depths. Using a polycrystal of GaAs, Zn diffused for 10 minutes at 500°C the local variation of V_c was observed by scanning the device surface with a fine tungsten point while the crystal was illuminated. Preliminary results give $L \approx 1$ mm, in agreement with other rough estimates. A twin boundary showed no local effect on V_{oc} .

A similar experiment was done by evaporating CuI (see below) onto another GaAs crystal containing small angle grain boundaries. In this case, no drop in V_{oc} was found near these boundaries.

III. BARRIER CELLS

The difficulties encountered with polycrystalline cells, outlined above and in the previous quarterly report lead us to consider cells employing isolated powder particles. There are two main problems in such an approach:

1. Mounting a layer (preferably a single layer) of particles on or in a matrix which makes ohmic contact with one side of the particles and,
2. Making a junction in, or barrier contact to the other side of the particles, with appropriate electrical connections, and insulation as obviously required.

A start has been made upon the first part, (1), of this problem by pressing GaAs particles into soft aluminum sheet, which is subsequently given an anodic oxidation treatment. One hopes that the tops of the particles are thereby insulated from the bottoms which are in contact with the aluminum.

Suppose now that step (2) above has been performed and that η_p is the average conversion efficiency per particle and that p is the ratio of particle cross section to cell cross section perpendicular to the illumination. Then the cell efficiency η_c is limited as $\eta_c \leq p \eta_p$. (1)

Potential methods for forming a junction or barrier should therefore be tested on single crystal material, both because it will be simpler to perfect the necessary techniques, and also because Eq. (1) requires $\eta_p > \eta_c$, and η_p can be approximated by measuring the efficiency of single crystal cells.

Where the barrier-forming step follows that of mounting the particles in a matrix, there will generally be temperature limitations on the barrier-forming processes. These considerations lead to the study of cuprous iodide (CuI) on GaAs. CuI is a p-type semiconductor. It is transparent to approximately 2.8 - 3.0 ev.

Its properties have been recently reviewed by Herrick and Tevebaugh* who also give references to earlier literature. CuI forms a rectifying and photovoltaic barrier with n-type GaAs. In this respect, it behaves as though it forms an inversion layer on the GaAs and makes an ohmic contact to this layer. Hence, we refer to the system as a "barrier" and not a "hetero-junction".

CuI can be formed on GaAs by three methods:

1. Vacuum evaporation of CuI,
2. Vacuum evaporation of Copper, and the subsequent exposure of the copper layer to iodine vapor,
3. Electrodeposition of copper, and the subsequent exposure of the layer to iodine vapor.

The value of V_{oc} obtained with a CuI/GaAs barrier depends on the chemical history of the GaAs crystal up to the time at which the Cu or CuI is deposited on it. Various approaches have been tried followed by method (3) above, since the electrodeposition method is the fastest one for producing an experimental cell. The highest values of V_{oc} have been over 0.8v for small area barriers. These have been produced with pre-treatments which were designed to minimize the amount of oxide left on the GaAs crystal prior to the Cu deposition.

The value of I_{sc} depends not only on the pre-treatment of the GaAs, but also on the optical transmission and lateral sheet resistance of the CuI layer. These depend on more than the thickness of the CuI layer.

*C.S. Herrick and A.D. Tevebaugh, J. Electrochem.Soc. 110,119 (1963).

Work elsewhere in these Laboratories is currently aimed at understanding and controlling the properties of the CuI layers.

The value of I_{sc} also depends on the gridding of the cell. Using a simple U-shaped grid, values of $V_{oc} = 0.79$ volt and $I_{sc} = 17$ ma have been obtained under microscope light illumination. However, the estimated sunlight efficiency of a similar cell was below 1%.

It is possible that a barrier cell will have better performance than a homojunction cell when made on polycrystalline material. As noted above, small angle grain boundaries did not locally lower V_{oc} in a CuI/GaAs cell. In preliminary studies, CuI/polycrystalline GaAs cells have shown very little rectification.

Other approaches to the barrier type cell have begun. Thin layers of Cu were deposited on n-GaAs single crystals and air fired. The chemistry is not understood. A layer forms which does not behave like any of the copper oxides. A Cu/GaAs barrier gives about 0-3 v for V_{oc} . After firing $V_{oc} = 0.8$ v and $I_{sc} = 5$ ma have been observed.

This technique, when applied to a polycrystalline n-type GaAs film, has yielded $V_{oc} = 0.5$ v and $I_{sc} = 1.2$ ma, and a V-I characteristic showing better rectification than has been observed with grown p-n junctions on such films.

IV. GALLIUM PHOSPHIDE

The work in this area has aimed at the production of GaP/GaAs heterojunctions.

In the course of the work, further information has been obtained on the GaP growth process.

To obtain conducting layers of GaP reproducibly, it is now clear that both the geometry of the apparatus and the temperatures of the source crystal and substrate require close control. The temperature difference between the source and substrate must be less than 50°C.

It has been found that conducting GaP films show red photoluminescence at liquid nitrogen temperature. If the luminescence is absent or dim, the conductivity is low.

In this, as in other barrier studies, it is convenient, where possible, to start with single crystal material. A series of n-GaP on p-GaAs single crystal barriers were made under identical conditions but with increasing times of deposition. V_{oc} became lower for thicker GaP deposits. It dropped from 0.55 v at 20 microns to about 0.1 v at 45 microns thickness of GaP. This would not be expected if an ideal heterojunction were being formed. One possibility is that the junction is formed deeper in the GaAs as time goes on at the high temperature.

On the other hand, when this experiment was repeated with a smaller temperature difference between the source and the substrate GaAs (and using another furnace) V_{oc} remained approximately 0.6 v for thickness in the range 120 to 250 microns.

Similar barrier cells made on polycrystalline GaAs show less rectification, particularly when illuminated. If the junction lies wholly within the GaAs layer, this result would be expected.

FUTURE PLANS

We will attempt to get more quantitative information on the effect of the intercrystalline boundaries on cell performance.

The work on CuI and other barrier-forming materials will be continued and applied to polycrystalline and powder deposits when the performance on single crystal GaAs looks promising.

Attempts will be made (by measuring the spectral response, for example) to get a better understanding of GaP/GaAs barriers, and also to further refine the growth of GaP layers.

CONCLUSIONS

The work of this quarter gives further support to the view that leakage at intercrystalline boundaries is the major factor which limits the efficiency of polycrystalline GaAs solar cells.

As a result, we further conclude that more attention should be focussed on barrier-type cells - on either polycrystalline or powder semi-conductors.

It is concluded that the GaP/GaAs junctions made to date consist of barriers, rather than heterojunctions.